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The hydrophobic effect Gibbs energy

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Abstract

A new method of experimental determination of thermodynamic functions of the hydrophobic effect is proposed. It is based on regarding the thermodynamic functions of hydration as the sum of thermodynamic functions of nonspecific hydration, specific hydration and the hydrophobic effect. In addition to the previously developed method to determine the hydrophobic effect enthalpies, we present a new method to calculate the hydrophobic effect Gibbs energies. The hydrophobic effect Gibbs energies of noble and simple substance gases, alkanes, arenes, and their halogenated derivatives are determined. For all the compounds studied, the hydrophobic effect Gibbs energy is found to be positive. From the values of the Gibbs energies and the enthalpies of the hydrophobic effect, the entropies of the hydrophobic effect are calculated. They are found to be negative for all the compounds. An excellent linear correlation between the hydrophobic effect Gibbs energy and McGowan characteristic molecular volume of the solute is found. The method was applied to a large molecule of fullerene C_{60}. The hydrophobic effect Gibbs energy of fullerene does not deviate from the linear dependence observed for small solutes.

Keywords: Hydrophobic effect; Hydrophobicity; Hydration; Solvation; Gibbs energy

1. Introduction

Hydrophobicity is an important factor that plays a significant role in various chemical, physical and biological processes [1–3]. It determines the stability of biological membranes, globular proteins, micelles, and governs the distribution of compounds in live organisms [4–7]. Although the hydrophobic effect is a well-known and extensively studied phenomenon it still is not thoroughly explained.

The studies of the hydrophobicity can be based on the analysis of thermodynamic functions of solution in water either focus on the solvent-induced interactions between apolar molecules or moieties in water. The following anomalies of thermodynamic functions are observed for the hydrophobic solutes in water: 1) large positive values of the Gibbs energy of hydration, dissolution in water, and transfer from an apolar solvent to water over a wide temperature range; 2) large negative entropies of hydration at 298 K rapidly growing up as the temperature increases; 3) large positive heat capacities of hydration [8]. In most of the studies (this includes simulation and scaled particles theory studies) these thermodynamic functions (Gibbs energy, enthalpy, entropy, and heat capacity) are considered directly. However, some researchers try to determine the contribution of the hydrophobic effect to the thermodynamic functions of hydration. This contribution is considered as the measure of the "special" properties of water in comparison with the other solvents.

The differences between the thermodynamic functions of hydration and solvation in a reference solvent are often used as the quantitative characteristics of the hydrophobic effect. The reference solvent is supposed to model water "in the absence of hydrophobicity". For example, thermodynamic functions of transfer from liquid alkane into water are sometimes meant to be thermodynamic functions of the hydrophobic effect [9]. The most widely used parameter of hydrophobicity, the octanol–water partition coefficient (log P) [10], is related to the Gibbs energy of transfer from octanol into water phase. In these approaches it is tacitly assumed that the partial molar thermodynamic functions

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